Poly(ethylene-co-1,4-cyclohexylenedimethylene terephthalate) Copolyesters Obtained by Ring Opening Polymerization

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ABSTRACT: Cyclic oligomer fractions of ethylene terephthalate c(ET)n and 1,4-cyclohexylenedimethylene terephthalate c(CT)n were obtained by yclodepolymerization of their respective polyesters, the former containing around 80 mol % of trimer and the latter with around 70 mol % of trimer to pentamer. Mixtures of these fractions at selected compositions were subjected to ring opening copolymerization to give a series of poly(ethylene-co-cyclohexylenedimethylene terephthalate) copolyesters with ET/CT comonomer ratios ranging from 90/10 to 10/90. The copolyesters were characterized by GPC and NMR, and their thermal properties were evaluated by DSC and TGA. They had essentially the same composition as the feed from which they were produced and had an average-weight molecular weights between 30,000 and 40,000 g/mol with polydispersities between 2 and 2.7. The distribution of the monomeric units in these copolyesters was essentially at random although it evolved to be a blocky microstructure as the contents in the two comonomers became more dissimilar. Their thermal behavior was the expected one for these types of copolyesters with crystallinity and heating stability decreasing with the content in CT units.

Keywords: *aromatic copolyesters; cyclodepolymerization; PCT; PET; PETG; ring opening polymerization (ROP)*

INTRODUCTION

It is a well known fact that minor amounts of cyclic oligoesters (<2 wt %) are unavoidably generated in the step-growth polycondensation of aromatic polyesters such as poly(ethylene terephthalate) (PET). [1–3] The presence of such cycles in the produced polyesters has detrimental effects on the mechanical and optical behavior of the material due to their plasticizing and nucleating properties. [4,5] Paradoxically cyclic oligoesters are receiving greater attention nowadays because of their interest as monomers for the synthesis of linear polyesters via ring opening polymerization reaction (ROP). [6–8]. Clear advantages offered by ROP compared to classical polycondensation procedures are the low melt viscosity and high reactivity displayed by the cyclic compounds used as monomers, and the absence of by-products in the polymerization reaction. These features are largely convenient for reaction-processing making ROP of cyclic oligoesters, a method suitable for the manufacture of polyester products by reaction injection molding and composite reaction molding. [9–11] Two methods are currently available for the production of the cyclic oligoesters needed for the synthesis of polyesters by ROP, that is, condensation of diols with diacid chlorides and heatinginduced cyclodepolymerization of linear polyesters. [12–16] The latter has become particularly useful for the preparation of alkylene phthalate cyclic oligomers from industrial thermoplastic polyesters like PET, [4,10,11,17] poly(butylene

terephthalate), [18,19] and poly(ethylene isophthalate). [20] The procedure, which has been studied in detail by several authors, is based on the ring-chain equilibrium reaction that takes place by heating the polyester at high dilution affording cyclic oligomer fractions in good yields. As a consequence, ROP is starting to be considered a serious alternative to the traditional polycondensation method for the preparation of the most-extensively used aromatic polyesters. The ROP method has been successfully extended to the synthesis of copolyesters made up of aromatic and aliphatic units as PET with lactones [21,22] and lactides, [23] poly(butylene terephthalate-co-caprolactone), [24] and poly(hexamethylene-co-caprolactone) [25] prepared from e-caprolactone and cyclic oligomers of butylene terephthalate and hexamethylene terephthalate, respectively. A valuable up-dated account of the synthesis and polymerization of cyclic oligoesters has recently been reported by Brunelle. [26]

PET is a classical engineering thermoplastic that is produced in huge amounts to be used mainly as fiber and in blowing-injection molding. New tendencies that point toward PET copolyesters with modified properties are able to satisfy new market demands.[27] It was in 1959, at Tennessee Eastman, when Kibler et al. [28] found that very slowly crystallizing copolyesters were formed when dimethyl terephthalate (DMT) was polymerized with mixtures of 1,4-cyclohexy-lenedimethanol (CHDM) and ethylene glycol (EG). Thus, PET copolyesters in which about 30 mol % of EG is replaced by CHDM and known as PETG (name given by Eastman Chemical) are specialties able to cover applications where an extremely low crystallinity is needed without detrimental in mechanical properties. Nowadays, PETG copolyesters are industrially produced by polycon-densation of terephthalic acid or DMT with mixtures of EG and CHDM. [28]. The resulting copolyesters must have a fair high molecular weight and a homogeneous microstructure to fulfill the technical specifications required for processing and applications. In this study, we have explored the possibility of obtaining these CHDM containing PET copolyesters by ROP. Fractions of cyclic oligomers of ethylene terephthalate c(ET)n and 1,4-cyclohexylenedimethylene terephthalate c(CT)n are obtained by cyclodepolymerization and properly characterized. Mixtures of these fractions at selected compositions are copolymerized via ROP to give poly(ethylene-co-1,4-ciclohexylenedimethylene terephthalate) copolyesters (abbreviated as coPExCyT where x and y indicate the mol % of ET and CT units in the copolyester) with a wide range of comonomer compositions. The chemical structure and microstructure of these copolyesters are characterized by NMR and their thermal properties are evaluated by DSC and TGA.

EXPERIMENTAL

DMT (99%), 1,4-cyclohexanedimethanol (CHDM) (99%, cis/trans 30/70), dibutyltin oxide (DBTO) (98%), 1,2-dichlorobenzene (DCB) (99%) trifluoroacetic acid (TFA) (99%), and trichlorobenzene (TCB) (99%), were purchased from Sigma-Aldrich and were used without further purification. Tetrabutyl titanate (TBT) (Merck-Schuchardt) and antimony (III) oxide (Sb2O3) (97%, Panreac) were reagent grade and used as received. The solvents used for purification and characterization purposes, such as chloroform, dichloromethane (DCM), methanol, diethyl ether, dichloroacetic acid (DCA), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were high-purity grade and used as received. High-performance liquid chromatography (HPLC)-grade solvents (DCM, hexane, and 1,4-dioxane) used for the chromatographic analysis were supplied by Panreac. The PET sample (Tg: 80ºC, Tm: 245ºC) in the form of pellets (~2 × 3 × 4 mm) was a gift of Artenius Prat (El Prat de Llobregat, Barcelona). A 0.1% w/v solution of this sample in DCA at 25ºC had an inherent viscosity of 0.62 dL/g.

Measurements

^{1}H and ^{13} CNMR spectra were recorded on a Bruker AMX-300 spectrometer at 25ºC operating at 300.1 and 75.5 MHz, respectively. Both polyesters and cyclic compounds were dissolved in deuterated chloroform either pure or mixed with TFA, and spectra were internally referenced to tetramethylsilane. About 10 and 50 mg of sample in 1 mL of solvent were used for ^{1}H and ^{13}C, respectively. Sixty-four scans were recorded for ^{1}H, and between 1000 and 10,000 scans for ^{13}C NMR, with 32 and 64 K data points and relaxation delays of 1 and 2 s, respectively.

HPLC analytical analysis was performed at 25ºC in a Waters apparatus Equipped with a UV detector of Applied Biosystems operating at 254 nm wavelength and a Scharlau Science column (Si60, 5 µm; 250 X 4.6 mm). Cyclic oligomers (1 mg) were dissolved in DCM (1 mL) and eluted with hexane/1,4-dioxane by the combination of a gradient and an isocratic mode at a flow of 1 mL/ min. A Waters Delta 600 HPLC system was used for semipreparative work for separation and collection of the different product fractions. The system comprised a 600E piston pump, Waters 996 photodiode array detector controlled by a 600E system, and a Waters Fraction Collector III. The separation was carried out using a SunFire column (Silica, 10 µm; 250 x19 mm) and varying ratio hexane:1,4-dioxane mixtures at a flow rate of 17 mL/min and UV detection at 254 nm. Data handling and treatment were performed on Empower software (Waters).

Molecular weight analysis was performed by GPC using HFIP containing sodium trifluoroacetate (6.8 g/L) as mobile phase in a Waters equipment provided with RI and UV detectors; 100 µL of sample solution (0.1% w/v) was injected and

chromatographed with a flow of 0.5 mL/min. A HR5E Waters linear Styragel column (7.8 x 300 mm^2, pore size 10^3 –10^4 A) packed with crosslinked polystyrene and protected with a precolumn (VanGuard, 1.8 µm, 2.1x5 mm) was used. Molecular weight averages and distributions were calculated against PMMA standards. Intrinsic viscosities were measured from polymer solutions in DCA using an Ubbelohde viscometer thermostatted at 25.0 ± 0.1ºC. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded in a 4700 Proteomics Analyzer instrument (Applied Biosystems) of the Proteomics Platform of Barcelona Science Park, University of Barcelona. Spectra acquisition was performed in the MS reflector positive-ion mode. About 0.1 mg of sample was dissolved in DCM (50 µL) and 2 µL of this solution was mixed with an equal volume of a solution of anthracene in DCM (10 mg/mL) and the mixture left to evaporate to dryness onto the stainless steel plate of the analyzer. The residue was then covered with 2 µL of 2,5-dihy-droxybenzoic (DHB) matrix solution [10 mg of DHB suspended in 1 mL of solution of acetonitrile/water (1/1) with 0.1% TFA] and the preparation left to dry prior to the exposure of the laser beam.

The thermal behavior of cyclic compounds and polymers was examined by differential scanning calorimetry (DSC), using a Perkin–Elmer DSC Pyris 1 apparatus. Thermograms were obtained from 4 to 6 mg samples at heating and cooling rates of 10ºC/min under a nitrogen flow of 20 mL/min. Indium and zinc were used as standards for temperature and enthalpy calibration, respectively. Glass transition temperature (Tg) was taken as the inflection point of the heating DSC traces recorded at 20ºC/min from melt-quenched samples and melting temperature (Tm) was taken as the maximum of the endothermic peak appearing on heating traces.

Polymerization and Cyclodepolymerization Reactions.

Synthesis of PCT by Polycondensation

This polymer was synthesized to be used as source for 1,4- cyclohexylene-dimethylene terephthalate cyclic oligomers. It was prepared by polycondensation of CHDM and DMT according to the procedure described in the literature, [20] with minor modifications. CHDM (48.99 g, 0.34 mol) and DMT (30 g, 0.154 mol), that is, with a molar ratio of 2.2:1, were introduced into a 199 mL three-necked round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a vacuum distillation outlet. The temperature was raised to 190ºC and, after complete homogenization of the mixture, ~0.6 mmol of TBT catalyst per mol of DMT was added. Transesterification was carried out under a low nitrogen flow for a period of 5 h with formation of methanol. The temperature was then raised to 290ºC and the pressure reduced to 0.5–1 mbar, and the polycondensation reaction was allowed to proceed isothermally under these conditions for 120 min. The reaction mixture was then cooled to room temperature, and the atmospheric pressure was recovered with a nitrogen flow to prevent degradation. The solid mass was dissolved in a mixture of chloroform/TFA (9/1), and then, the polymer precipitated with cold

diethyl ether was collected by filtration and washed thoroughly with cold diethyl ether. All samples were dried at 60ºC under reduced pressure for a minimum of 24 h before use (25.5 g, 85% yield).

^{1}H NMR (CDCl3/TFA, 300.1 MHz) δ: 1.21, 1.98, 1.63, 1.73 (4m, 8H), 1.87, 2.12 (2m, 2H), 4.27, 4.38 (2d, 4H), 8.14 (s, 4H). ^{13}C NMR (CDCl3/TFA, 75.5 MHz) δ: 25.2, 28.7, 34.4, 36.9, 69.4, 71.5, 129.7,133.9, 168.0.

Synthesis of Cyclic Oligomers by Cyclodepolymerization.

The cyclic oligomers fractions c(ET)n and c(CT)n were obtained by cyclodepolymerization reaction of PET and PCT, respectively. The procedure previously described by Hodge et al.4 was used here for the preparation of c(ET)n. Five grams (26.0 mmol) of PET pellets, and 200 mL of DCB containing 3 mol % DBTO were introduced in a round flask equipped with a condenser. The mixture was refluxed at 180ºC for 48 h under vigorous stirring, cooled at 60ºC, and the insoluble material filtered off (1.2 g, 24%). The clear solution was evaporated to dryness at 70ºC and reduced pressure leaving a residue (3.8 g, 76%) that was then dissolved in chloroform and precipitated with diethyl ether. The precipitate was dispersed in DCM, and the insolubilized remaining material was removed by filtration and the solution was precipitated with diethyl ether. The c(ET)n fraction was collected as a white powder and dried at 60ºC under reduced pressure before use.

^{1}H NMR (CDCl3, 300.1 MHz) δ: 4.7 (s, 4H), 8.10 (s, 4H). 13C NMR (CDCl3, 75.5MHz) δ: 62.7, 129.7, 133.7, 165.2.

A similar procedure was used for the preparation of c(CT)n fraction. PCT (5.21 g, 19.0 mmol previously dried overnight in a vacuum oven at 60ºC) and 190 mL of TCB containing 3 mol % DBTO were introduced into a 250 mL round-bottom flask equipped with a condenser. This mixture was stirred vigorously, and the cyclodepolymerization reaction was allowed to proceed under reflux at 214ºC for 7 days. The mixture was cooled to room temperature and then filtered. The TCB was rapidly evaporated under vacuum at 80ºC to dryness, and the recovered solid (1.1 g, 21.3% yield, crude cyclic product) was dissolved in chloroform and precipitated with cold diethyl ether. The precipitate was recovered by filtration and re-precipitated from dichloromethane with diethyl ether (0.78 g, 15% weight). The cyclic oligomers were dried at 50ºC under reduced pressure for 48 h previous to characterization.

^{1}H NMR (CDCl3/TFA, 300.1 MHz) δ: 1.17, 1.94, 1.64 (3m, 8H), 1.82, 2.1 (2m, 2H), 4.20, 4.30 (2d, 4H), 8.10 (s, 4H). 13C NMR (CDCl3 /TFA, 75.5 MHz) δ: 25.4, 28.9, 34.6, 37.2, 68.0, 70.1, 129.5, 134.1, 165.8.

Synthesis of PET and PCT by Ring Opening Polymerization

The ring opening polymerization procedure was the same for both c(ET)n and c(CT)n cyclic oligomers. oligomers. Here, the description for the latter, cyclic oligomers (0.8 mmol) and Sb2O3 catalyst (0.5 mol %) were mixed by dissolving them in DCM and then by evaporating slowly the solvent under vigorous stirring. The residue was dried at 50ºC under reduced pressure for 24 h. The mixture was introduced into a two-necked round-bottom flask, purged with nitrogen to remove all traces of moisture and residual air, and then it was immersed into a bath at 290ºC. Polymerization was carried out at this tempe-rature for a period of 20 min under a nitrogen atmosphere. Finally, the reaction mixture was quenched in an ice-water bath, and atmospheric pressure was recovered using nitrogen to prevent degradation. The resulting polymer was dissolved in chloroform/TFA precipitated with cold diethyl ether and dried at 50ºC under reduced pressure for 48 h before characterization. PET: (0.197 g, 98.5% yield).

^{1}H NMR (CDCl3/TFA, 300.1 MHz) δ: 4.78 (s,4H), 8.12 (s, 4H). ^{13}C NMR (CDCl3/TFA, 75.5 MHz) d: 63.8, 130.0, 133.4, 167.4. PCT: (0.194 g, 97% yield). 1H NMR (CDCl3/TFA, 300.1 MHz) δ: 1.21, 1.98, 1.63, 1.73 (4m, 8H), 1.87, 2.12 (2m, 2H), 4.27, 4.37 (2 days, 4H), 8.14 (s, 4H). ^{13}C NMR (CDCl3/TFA, 75.5 MHz) δ: 25.2, 28.7, 34.4, 36.9, 69.4, 71.5, 130.0, 133.9, 168.1.

Synthesis of Poly(ethylene-co-1,4-cyclohexylenedimethylene terephthalate) Copolyesters (coPExCyT) by Ring Opening Polymerization

Copolyesters coPExCyT were obtained by ROP reaction of a mixture of c(ET)n and c(CT)n cyclic oligomers, where x and y denote the molar feed ratio of c(ET)n and c(CT)n, respectively. x moles of c(ET)n, y moles of c(CT)n, and Sb2 O3 catalyst (0.5% mol) were dissolved in DCM (10% w/v), and the solution was evaporated slowly at room temperature and dried in a vacuum desiccator for 24 h; 3 g of sample was introduced in a three-necked round-bottom flask equipped with inlet and outlet of nitrogen and provided with magnetic stirring. The flask was heated at 285ºC and maintained at this temperature for 20 min under a nitrogen atmosphere. Cyclic oligomers melt and quickly react to form a viscous gel. The mixture was cooled at room temperature with a nitrogen flow to prevent degradation. Approximately 2.8 g (90–95%) of mass samples are recovered depending on the copolymer composition. PET-rich copolymers were whitish, 70/30 and 50/50 copolymers were transparent, and 30/70 and 10/90 copolymers displayed a pale yellow coloration.

RESULTS AND DISCUSSION

Synthesis and Characterization of Cyclic Oligomers c(ET)*n* and c(CT)*n*

The reaction of cyclodepolymerization of PCT was carried out mostly in both DCB and TCB at high dilution in their respective refluxing temperatures and using different reaction times with the aim of attaining maximum productivity. Table 1 shows the reaction conditions, yields, and compositions of the cyclic n-mers that were obtained in each case. c(CT)n were invariably obtained in very low yields compared to c(ET)n yields, very probably due to the stiff nature of the CHDM unit. The presence of this unit in the PCT chain not only decreases the solubility of the polymer that disfavors the depolymerization reaction but also increases the annular stress of small c(CT)n making them more difficult to form.

The cyclic oligomers obtained by cyclodepolymerization were purified by re-dissolution in chloroform and reprecipitation with diethyl ether, and they were characterized by combining HPLC, MALDI-TOF, and NMR spectroscopy. The absence of any trace of end group signals in the 1H NMR spectra of the purified fraction (Fig. 1) indicates that the content in open chain oligomers must be very small, a fact that is consistent with the full solubility in chloroform displayed by such fraction. The ^{1}H NMR additionally revealed that the cis/trans CHDM units ratio in this fraction was near to 40/60, which is significantly higher than the 30/70 ratio present in both the PCT polyester used for cyclodepolymerization and in the CHDM monomer used for polycondensation with DMT. Such enrichment in cis configuration in the cyclic fraction may be explained by taking into account its more favorable geometry for small size cycle formation compared with the trans configuration. Figure 2 shows the MALDI-TOF spectra of c(ET)n and c(CT)n fractions that were used for identifying the oligomeric sizes present in these two fractions, as well as their respective HPLC chromatograms, which were used for determining the amount present of each population. Data afforded by these analyses are compared in Table 1 showing that they are composed mainly of oligomeric sizes ranging from 2 to 7 repeating units with the cyclic trimer being the predominant compound by far in both fractions. Furthermore, no significant differences in composition were observed for the different conditions used for preparation.

Thermal data of c(ET)n and c(CT)n fractions provided by DSC and TGA analysis are given in Table 1. Thermogravimetry of the c(CT)n fraction revealed that these cycles start to decompose upon heating above 390ºC with the maximum decomposition rate taking place in the proximities of 420ºC and that they leaves around 5% of residue after being heated at 500ºC. The c(ET)n fraction appears to be about 20–30ºC more stable and it leaves about 15% of residue. The DSC analysis of these fractions combined with the GPC analysis of the heated samples afforded valuable information about their polymerizability. As it is depicted in Figure 3(a,b), the traces of both c(ET)n and c(CT)n samples coming from synthesis show an endothermic peak close to 200ºC followed by another one appearing at 267ºC and 304ºC for the respective cases. The evolution of the molecular weight of the molten samples with temperature at a

heating rate of 10ºC/min is depicted in Figure 3(c) showing that at 260ºC they have a number-average polymerization degree of 20–30, which increases up to around 50 when temperature approaches to 300ºC. These results reveal that both c(ET)n and c(CT)n are able to polymerize fast in the absence of catalyst at relatively low temperatures. The second endothermic peak seen on the DSC heating traces must arise therefore from the melting of PET and PCT, respectively. As expected, crystallization and remelting of the polyesters take place upon cooling and reheating, the melting temperatures observed in the later case being largely affected by the thermal history of the samples.

Ring Opening Polymerization of Cyclic Oligomers c(ET) and c(CT)

First, ring opening polymerization of c(ET)n and c(CT)n were carried out separately for comparison, and results obtained therein are given in Table 1. Yields and molecular weight distributions were similar in the two cases and their thermal properties were in full agreement with what should be expected for these well-known homopolyesters and according to their respective molecular sizes.

Synthesis of Poly(ethylene-co-1,4-cyclohexylenedimethylene terephthalate) Copolyesters

coPExCyT copolyesters were prepared by ring opening polymerization from mixtures of c(ET)n and c(CT)n cyclic oligomers according to Scheme 1 and the obtained results are listed in Tables 2 and 3. The copolymers were obtained in good yields as white solids that slightly yellowed as their content in CT units increased. The evolution of the molecular weight with the advance of the reaction was followed by GPC analysis of aliquots extracted at increasing reaction times and results are comparatively plotted in Figure 4 for the two homopolyesters PET and PCT, and the copolyester coPE70C30T. It is seen in this plot that the polymer size approaches to the maximum attainable at very early reaction stage and that polydispersity does not change significantly with time. The weight-average molecular weights of the copolyesters obtained at 285ºC for a reaction time of 20 min were between 30,000 and 50,000 g/mol with polydispersities oscillating between 2 and 3. Their ^{1}H and ^{13}C NMR spectra are in full agreement with the chemical structure expected for these compounds. The spectra recorded from the coPE70C30T copolyester with the indication of the assignments for all the signals are displayed in Figure 5 for illustration. The composition of the copolyesters could be accurately determined by the integration of oxymethylenic protons signals arising from the ET and CT units, which appear at 4.8 (peak *a*) and 4.4 (peaks *a*ʹ) ppm, respectively, in the 1H NMR spectra. In all cases, the final composition of the copolyester was found to be very close to that used in the feed with deviations being lower than 5%, which can be taken as indicative that the relative reactivities of the two oligomeric fractions must be similar. The splitting observed for the *a*ʹ signals, also observed for *e* and *f* signals, arises from the presence of the two configurations present for the CHDM ring with a cis/trans ratio of 37/63, which is close to the ratio observed for the cyclic oligomers c(CT)n. The weak signals

observed at 4.7 and 4.1 ppm in the 1H NMR spectra reveal the presence of diethylene glycol units in small amounts ranging between 0.5 and 1.5% along the copolyester series. The presence of these units in the copolyester is assumed to be a consequence of the formation of diethylene glycol by etherification of the EG at the temperatures used for the polymerization reaction.

The microstructure of the coPExCyT copolyesters was studied by ^{13}C NMR spectroscopy. The signals in the ^{13}C NMR spectrum of coPExCyT arising from the non-protonated aromatic carbons and the carbonyl carbons are shown in Figure 6. These two signals seems to split into four peaks due to their sensitivity to the sequence distribution at the level of dyads (ETE, CTC, and ETC/CTE) that may be present in the copolyester chain. The Lorentzian deconvolution of such peaks allowed estimating the dyad contents in the copolyesters. These experimental values were then used in the equations [30] displayed below to calculate the number-average sequence length of ET and CT units, nET and nCT, respectively, as well as the randomness (B) of the copolyester.

$$n_{ET} = \frac{N_{ETE} + \left(\frac{N_{ETC}}{2}\right)}{\left(\frac{N_{ETC}}{2}\right)} \quad n_{BEPT} = \frac{N_{CTC} + \left(\frac{N_{ETC}}{2}\right)}{\left(\frac{N_{ETC}}{2}\right)}$$

$$B = \frac{1}{n_{ET}} + \frac{1}{n_{CT}}$$

Theoretical values of nET, nCT, and B were calculated according to the Bernouillian statistics for copolyesters with the composition given in Table 2. Experimental and theoretical values obtained for whole series of coPExCyT are compared in Table 3 showing that they become closer as the contents in the two comonomers approach to each other. Thus, the degree of randomness is lower than 0.8 for copolyesters 10/90 and 80/20 whereas it is practically 1 for the 50/50 copolyester. The conclusion is therefore that the microstructure of coPExCyT obtained by ROP is essentially at random for copolyesters with similar compositions in the comonomers but that it evolves to a rather blocky microstructure as the comonomer ratio goes far from unity.

Thermal Properties of coPExCyT Copolyesters

The thermal properties of the copolyesters were examined by DSC and TGA. As it can be seen in Table 2, the thermal stability of coPExCyT decreased steadily in a range of 20ºC as the content in CT units in the copolymer increased with the maximum and minimum values corresponding to the parent homopolymers PET and PCT, respectively. This pattern of behavior is in agreement with preceding work published by Amari et al.,[31] in which the thermal degradation of these copolymers was studied by analyzing by NMR, the end groups present in the degraded products. They showed that thermal decomposition evolved

with releasing of unsaturated compounds that generated by cis-β-elimination and found that CT units were less stable to heating than the ET ones because the ester link between terephthalic acid and CHDM is thermally weaker than that between terephthalic acid and EG.

As expected, the crystallinity displayed by coPExCyT copolyesters was lower than in the parent homopolyesters. DSC traces recorded at heating and cooling from the melt are compared in Figure 7 for the whole series of coPExCyT as well as for PET and PCT, and thermal data extracted from this analysis are listed in Table 2. It is seen that copolyesters with low contents in either ET or CT units remained crystalline with both melting temperatures and enthalpies decreasing as the contents in the two comonomers approach to each other to the point that copolyesters with CT contents between 30 and 50 mol % were unable to crystallize. Copolymerization also hampered the crystallization process so that only copolyesters containing 10 mol % at maximum of any of the two comonomers were able to crystallize from the melt upon cooling at 10 _C/min [Fig.7(a)]. Furthermore, it was detected that the presence of CT units increased the crystallization temperature due to the more efficient nucleating effect played by relatively stiffer cyclohexylene structure. The amorphous window of compositions for the coPETxCTy copolyesters series extends from 20 to 70 mol % in CT, as it is illustrated in Figure 8. In addition, the glass transition temperature was slightly affected by the composition in ET and CT units as it should be expected for copolyesters with a random microstructure. As it is shown in Figure 8, Tg steadily increased from 80 to 88ºC for the coPExCyT series when going from PET to PCT.

CONCLUSIONS

In this study, it has been shown that the homopolyester poly(1,4-cyclohexylenedimethylene terephthalate) could be cyclodepolymerized by heating to render a cyclic oligomer fraction enriched in hexamethylene terephthalate trimer, tetramer, and pentamer cycles. The yield attained in this procedure was, however, significantly lower than usually attained in the cyclodepolymerization of other aromatic polyesters, which is probably due to the ring stress caused by the stiffness of the cyclohexane moiety. Cyclic oligomers of 1,4-cyclohexylenedimethylene terephthalate and ethylene terephthalate could be copolymerized by ring opening polymerization to produce copolyesters with practically the same comonomer compositions that were used in their corresponding feeds. The resulting copolyesters had fairly high molecular weights and a nearly statistical microstructure except for extreme comonomer ratios where it turned to be significantly blocky. These copolyesters displayed thermal transitions, thermal stability, and crystallinity according to their composition and in full agreement with those obtained by polycondensation. These results allow envisaging ring opening polymerization as a method suitable for the preparation of CHDM containing PET copolymers with similar structural features and properties to those obtained by the conventional polycondensation methods.

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TABLES & FIGURES

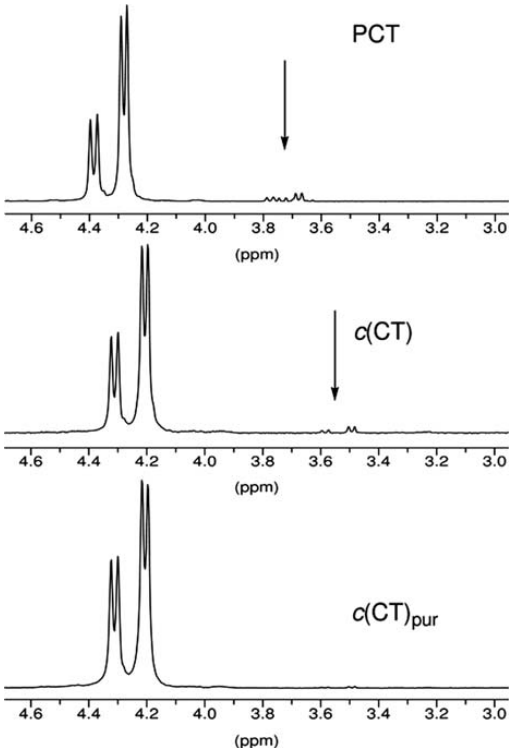

Figure 1. 1H NMR (CDCl3/TFA) spectrum of PCT obtained by polycondensation (top). 1H NMR (CDCl3) spectra of c(CT)n obtained by cyclodepolymerization before (middle) and after purification (bottom). The arrows point to the signals arising from CH2OH end groups.

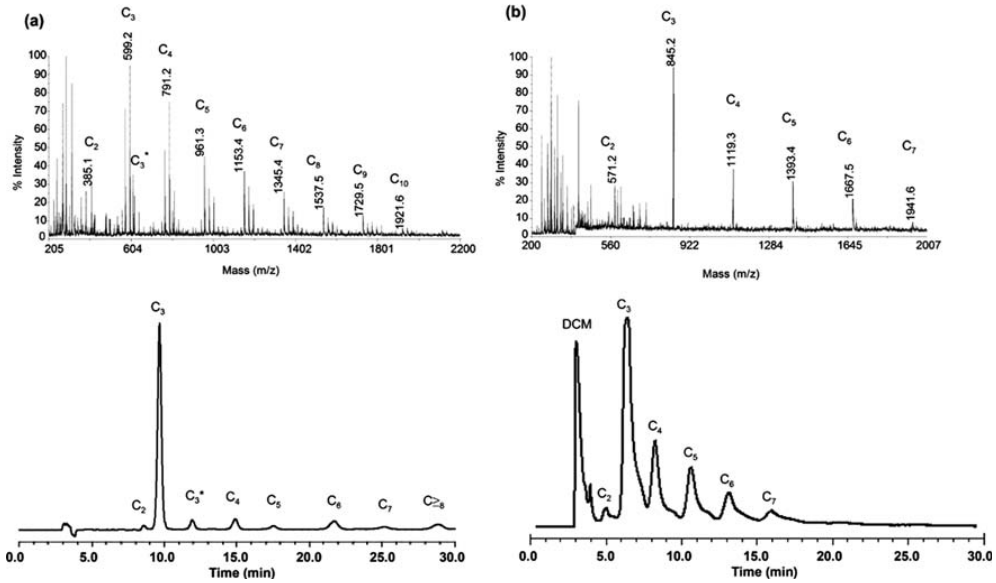

Figure 2. MALDI-TOF spectra (top) and HPLC chromatograms (bottom) of cyclic oligomers c(ET)n (a) and c(CT)n (b) prepared by cyclodepolymerization of PET and PCT, respectively. The MALDI-TOF highest intensity peaks corresponding to either protonated or Naþ ionized species are labeled; other unlabeled peaks arise from other undetermined ionized species coming from cyclic or lineal compounds. In the spectrum of c(ET)n, the peak labeled as C3* is attributed to diethylenglycol terephthalate cyclic trimer according to the previous study reported by Bryant and Semlyen. [17,18]

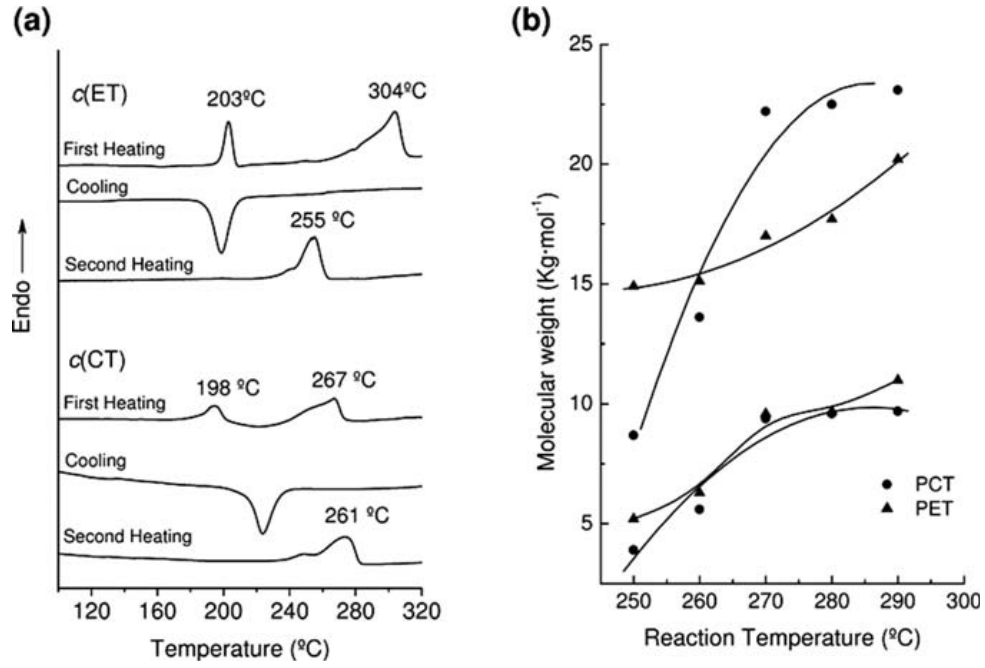

Figure 3. (a) DSC traces of c(ET)n and c(CT)n at heating and cooling. **(b)** Evolution of the molecular size of c(ET)n and c(CT)n with heating temperature. The heating/ cooling rate was 10ºC/min in all cases and no catalyst was added to the samples.

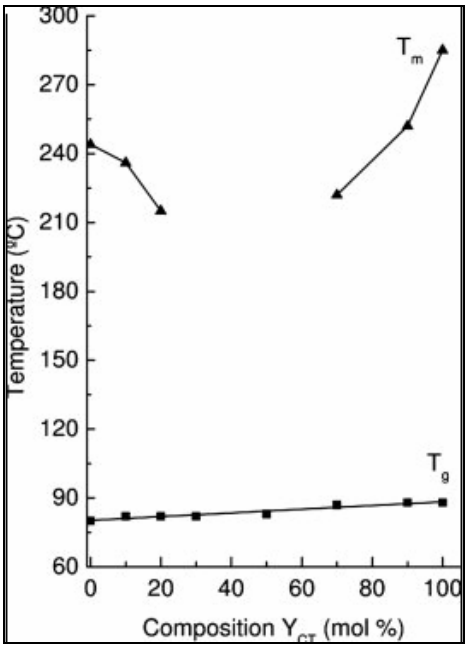

Figure 4. Evolution on the number- and weightaverage molecular weight of the resulting PCT, PET, and coPE70C30T obtained by ROP, as a function of reaction time.

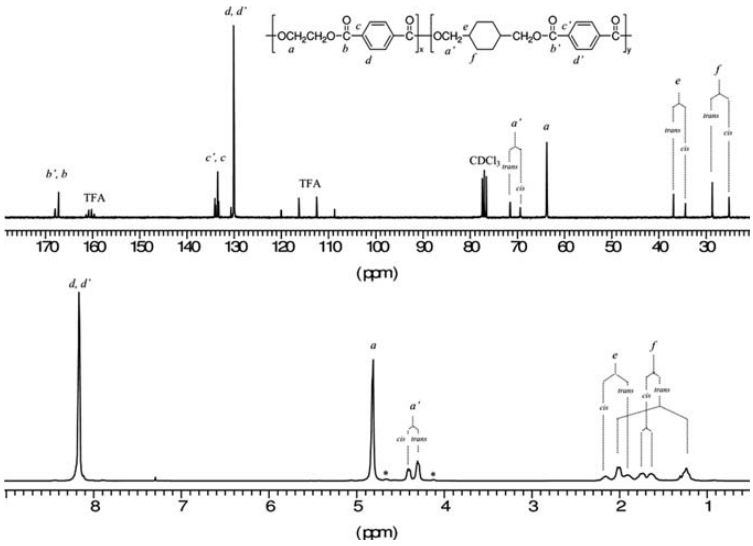

Figure 5. 1H NMR and 13C NMR spectra of coPE70C30T copolyester recorded in CDCl3/TFA (9/1) with the indication of peak assignments. *Signals arising from DEG units.

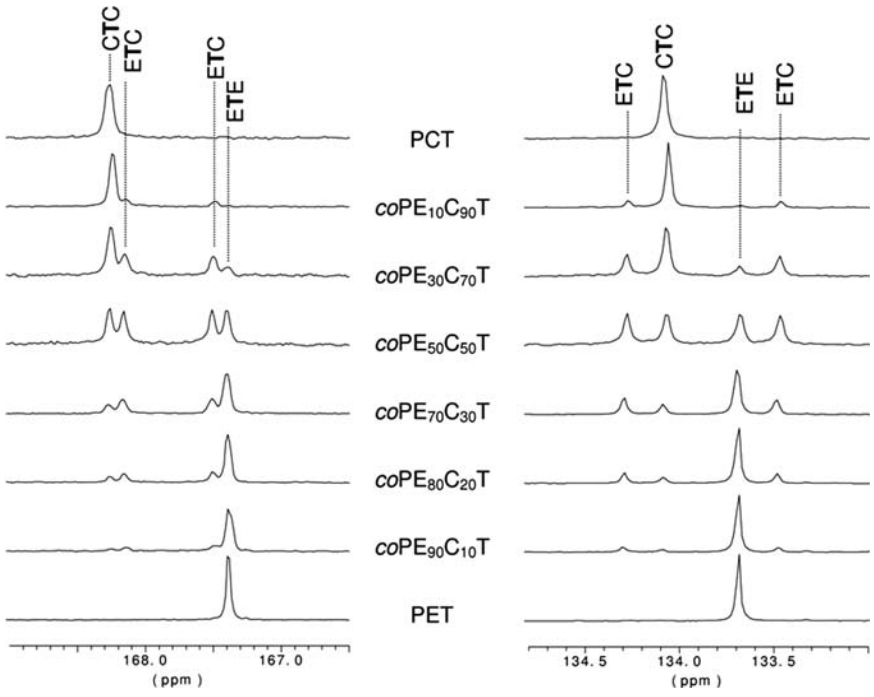

Figure 6. Carbonyl (left) and nonprotonated aromatic (right) carbon regions of the 13C NMR spectra of coPExCyT recorded in CDCl3/TFA (9/1) with the indication of the peak assignments referred to the possible dyads present in the copolyester chain.

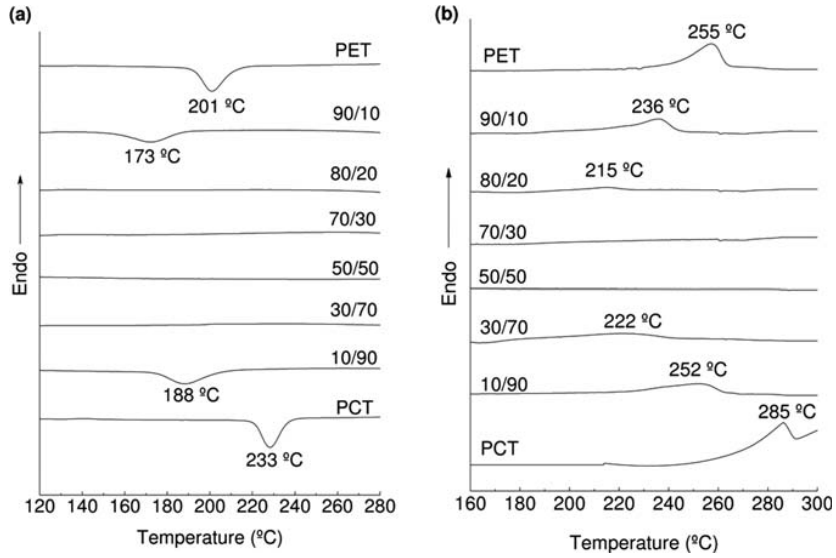

Figure 7. DSC traces of PET, PCT, and coPExCyT registered at 10ºC/min. **(a)** Coolingfrom the melt and **(b)** second heating.

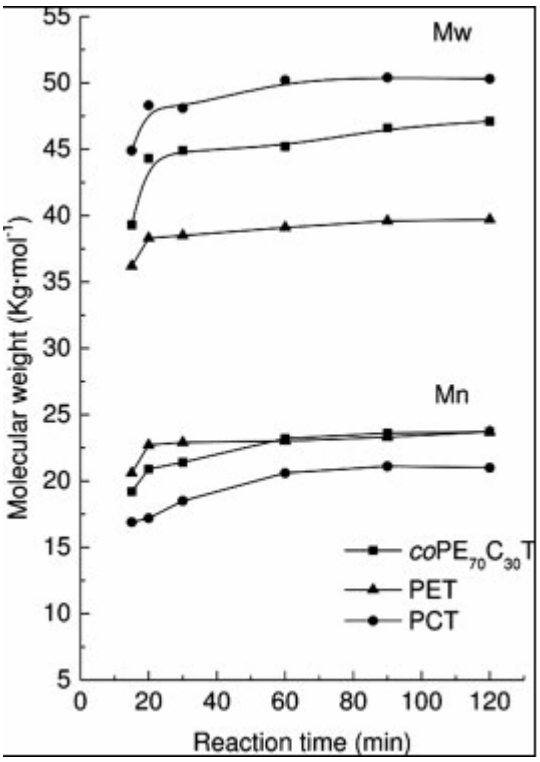

Figure 8. Evolution of melting point (Tm) and glass transition temperatures (Tg) of coPExCyT with the content in CT units

Table 1. Poly(1,4-cyclohexylenedimethylene terephthalate) and Poly(ethylene terephthalate): Polymerization and Cyclo-Depolymerization Results

Polycondensation																
Reaction Conditions					Molecular Size					Thermal Properties						
[DMT]/[CHDM][a]	TBT (mol %)	T (°C)[b]	t (min)[c]	Yield (%)	[η][d]	M_n[d]	M_n[e]	M_w[f]	PD[f]	T_g (°C)[f]	T_m (°C)[f]	°T_d (°C)[g]	T_d (°C)[g]	RW (%)[g]		
1:2.2	0.6	190/270	300/120	85	0.48	8.9	11.1	19.8	1.8	88	286	401	427	6		
Cyclodepolymerization of PET and PCT																
Reaction Conditions					Cycle Distribution[h]								Thermal Properties			
[Polyester][a]		Solvent[i]	T (°C)[c]	t (days)[c]	Yield (%)	1	2	3	4	5	6	7	≥8	T_g (°C)[f]	T_m (°C)[f]	°T_d (°C)[g]	T_d (°C)[g]	RW (%)[g]
PET	0.13	DCB	180	2	70	-	2	78*	6	3	5	2	4	-	203/304	416	454	15
PCT	0.05	TCB	214	7	20	-	3	59	16	12	7	3	-	-	196/268	394	425	5
	0.10	TCB	214	7	18	-	2	53	18	14	9	4	-	-	198/265	393	424	4
	0.10	TCB	214	10	20	-	2	57	15	13	9	4	-	-	198/267	393	423	5
	0.10	DCB	180	7	10	-	-	50	19	16	10	5	-	-	195/269	387	418	4
Ring-Opening Polymerization of Cyclic Oligomers																
Reaction Conditions					Molecular Size					Thermal Properties						
Polyester		Catalyst[j]	T (°C)[b]	t (min)[c]	Yield (%)	[η][d]	M_n[d]	M_n[e]	M_w[e]	PD[e]	T_g (°C)[f]	T_m (°C)[f]	°T_d (°C)[g]	T_d (°C)[g]	RW (%)[g]		
PET		Sb_2O_3	295	20	95	0.67	18	22.7	38.3	1.7	80	244	421	448	19		
PCT	1	TBT	290	20	95	0.53	10.9	15.8	38.2	2.4	86	272	396	424	6		
	2	DBTO	290	20	92	0.47	8.5	13.1	30.3	2.3	82	259	392	418	5		
	3	Sb_2O_3	290	20	97	0.58	13.2	17	48.1	2.8	88	285	402	428	6		
	4	Sb_2O_3	285	20	95	0.58	13.2	17.2	48.3	2.8	88	286	400	428	6		

a Molar ratio or molar concentration.
b Reaction temperatures (in polycondensation, for the two reaction steps used).
c Reaction times (in polycondensation, for the two reaction steps used).
d Intrinsic viscosity in DCA at 25 _C and number-average molecular weight determined from [g] using the Mark-Houwink parameters29 a ¼ 0.47 and K ¼ 67 _ 10_4.
e Molecular weight distribution (number and weight average molecular weight and polydispersity) determined by GPC.
f Glass transition and melting temperatures observed by DSC.
g Onset temperature (10% of weight loss), maximum rate decomposition temperature, and percentage of residual weight determined by TGA.
h Content in cycle sizes c(HT)n for n ¼ 2–7 as determined by HPLC and MALDI-TOF.
i Solvent used in cyclo-depolymerization reactions.
j Catalyst used for ring-opening polymerization at 0.5% mol relative to the monomer content.
*3 mol % of diethylenglicol terephthalate cyclic trimer was included.

Table 2. Copolyesters *co*PE$_x$C$_y$T by Ring-Opening Copolymerization of *c*(ET)$_n$ and *c*(CT)$_n$

Copolyester	[ET] / [CT][a]	% DEG[b]	[η][c]	M_w[d]	PD[d]	T_g[e] (°C)	T_c[f] (°C)	T_m[g] (°C)	ΔH_m[g] (J/g)	°T_d[h] (°C)	mT_d[h] (°C)	RW[h] (%)
PET	100/0	1.0	0.67	38,300	1.7	80	204	255	33.7	421	448	19
*co*PE$_{90}$C$_{10}$T	90.1/9.9	0.7	0.54	41,900	2.7	82	173	236	30.3	409	445	13
*co*PE$_{80}$C$_{20}$T	80.4/19.6	0.9	0.56	47,300	2.7	82	-	215	8.2	408	438	12
*co*PE$_{70}$C$_{30}$T	71.3/28.7	0.9	0.51	44,300	2.1	82	-	-	-	405	433	11
*co*PE$_{50}$C$_{50}$T	51.6/48.4	1.1	0.47	31,900	2.2	83	-	-	-	400	429	10
*co*PE$_{30}$C$_{70}$T	30.4/69.6	1.4	0.49	35,500	2.4	87	-	222	13.7	402	429	8
*co*PE$_{10}$C$_{90}$T	8.4/91.6	0.9	0.50	34,100	2.5	88	188	252	36.6	400	428	7
PCT	0/100	0	0.58	48,100	2.8	88	233	285	28.4	402	428	6

[a] Ethylene terephthalate/cyclohexylenedimethylene terephthalate molar ratio determined by ^{1}H RMN.
[b] Diethylenglicol terephthalate unit content determined by ^{1}H RMN.
[c] Intrinsic viscosity (dL/g) measured in dichloroacetic acid at 25 °C.
[d] Weight-average molecular weight and polydispersity determined by GPC.
[e] Glass transition temperature from melt-quenched samples determined by DSC at 20 °C/min.
[f] Crystallization temperature at cooling from the melt at 10 °C/min.
[g] Melting temperature and enthalpy determined by DSC on the second heating at 10 °C/min.
[h] Onset (10% of weight loss) and maximum rate decomposition temperatures, and residual weight determined by TGA under inert atmosphere.

Table 3. Experimental[a] and Theoretical (in parentheses) Sequence Distribution and Randomness of *co*PE$_x$C$_y$T Copolyesters

Copolyester	Dyads (mol %)			Average Sequence Lengths		Randomness B
	ETE	ETC	CTC	n_{ET}	n_{CT}	
*co*PE$_{90}$C$_{10}$T	79.6 (81.2)	16.4 (17.8)	4.0 (1.0)	10.4 (10.1)	1.5 (1.1)	0.77 (1.00)
*co*PE$_{80}$C$_{20}$T	65.8 (64.6)	25.2 (31.6)	9.1 (3.8)	6.2 (5.2)	1.7 (1.2)	0.74 (1.00)
*co*PE$_{70}$C$_{30}$T	52.2 (50.8)	35.1 (41.0)	12.7 (8.2)	4.0 (3.5)	1.7 (1.4)	0.83 (1.00)
*co*PE$_{50}$C$_{50}$T	25.7 (26.6)	48.7 (50.0)	25.6 (23.4)	2.1 (2.1)	2.0 (1.9)	0.97 (1.00)
*co*PE$_{30}$C$_{70}$T	11.1 (9.2)	40.4 (42.4)	48.4 (48.4)	1.5 (1.4)	3.4 (3.3)	0.95 (1.00)
*co*PE$_{10}$C$_{90}$T	3.9 (0.7)	16.7	79.4	1.5 (1.1)	10.5	0.78 (1.00)

.[a] Experimental values resulting by using the ^{13}C NMR data in the equations indicated in the text. Theoretical values were calculated on the basis of a Bernouillian dyad distribution for the copolyester composition data given in Table 2.

Scheme 1. Reactions involved in the preparation of coPExCyT copolyesters